Structural rigidity and thermal conductance of nanostructured carbon: nanotubes and foams

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14. ABSTRACT
Structural rigidity, phonon modes, and thermal conductivity of carbon nanostructures: nanotubes and graphitic foam.

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Outline

- **Motivation**

- **Computational Techniques**

- **Thermal Conductivity in Nanotubes**
  - Approaches and Pitfalls
  - Temperature Dependent Thermal Conductivity
  - Effect of Inter-Wall Interactions on Thermal Conductivity
  - Effect of Isotope Mixture on Thermal Conductivity

- **Low-Frequency Phonon Modes of Nanotubes**
  - Equilibrium Structure of Multi-Wall Tubes and Ropes
  - Soft Phonon Modes of Single-Wall Tubes
  - Libration and Rotation Dynamics of Interacting Tubes
  - Dynamics of Twistons and Orientational Melting

- **Hybrid Graphitic Foam**
  - Equilibrium Structure
  - Elastic Properties
  - Electronic Structure

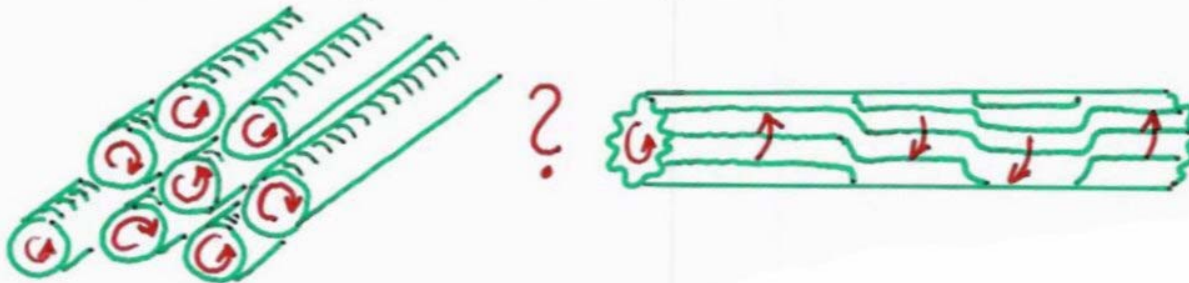- **Summary and Conclusions**

Motivation

- Can Nanotubes **conduct heat** well?
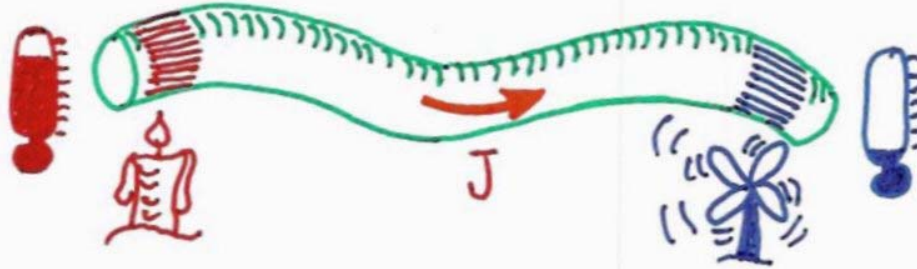
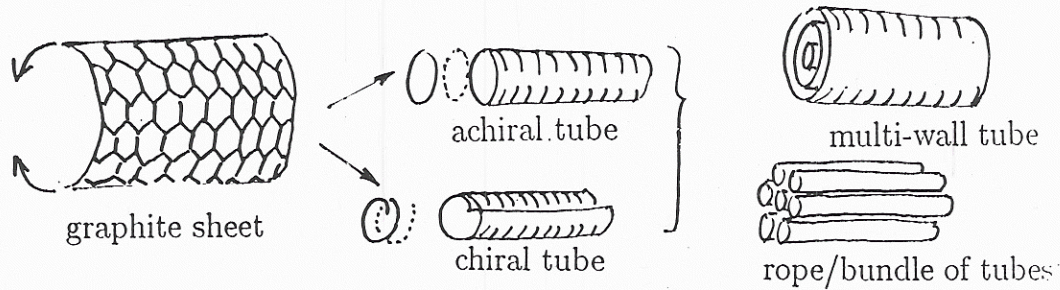- Which **Phonon Modes** limit Thermal Conduction?
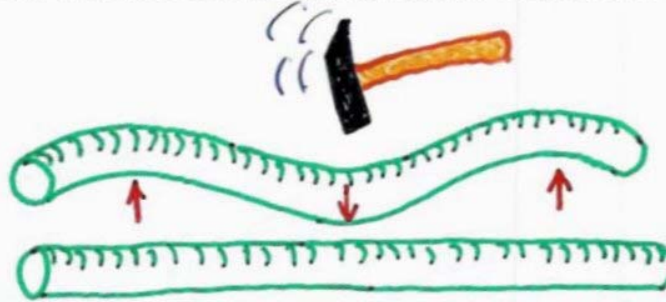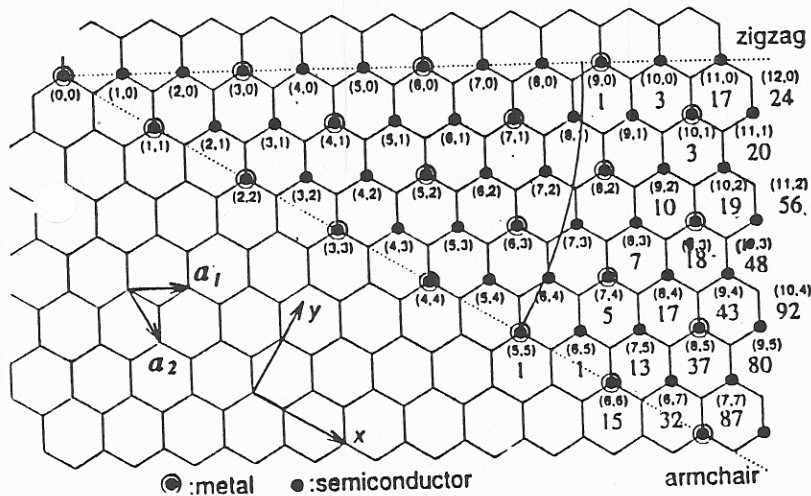

- Can interacting **Nanotubes Spin and Twist?**

- Is nanostructured carbon foam the ultimate structural and thermal material?

- **Structure of carbon nanotubes:**

graphite sheet

achiral tube

chiral tube

multi-wall tube

rope/bundle of tubes

- **Classification of carbon nanotubes:**

zigzag

(0,0) (1,0) (2,0) (3,0) (4,0) (5,0) (6,0) (7,0) (8,0) (9,0) (10,0) (11,0) (12,0)
1 3 17 24

(1,1) (2,1) (3,1) (4,1) (5,1) (6,1) (7,1) (8,1) (9,1) (10,1) (11,1)
3 20

(2,2) (3,2) (4,2) (5,2) (6,2) (7,2) (8,2) (9,2) (10,2) (11,2)
10 19 56

(3,3) (4,3) (5,3) (6,3) (7,3) (8,3) (9,3) (10,3)
7 18 48

(4,4) (5,4) (6,4) (7,4) (8,4) (9,4) (10,4)
5 17 43 92

(5,5) (6,5) (7,5) (8,5) (9,5)
1 1 13 37 80

(6,6) (6,7) (7,7)
15 32 87

a_1 a_2 x y

⊙ :metal   ● :semiconductor

armchair

$$\vec{R} = m\vec{a_1} + n\vec{a_2}$$

defines uniquely the (m, n) nanotube

- **Types of achiral nanotubes:**

(n, n): armchair nanotubes

$(n, 0)$: zig-zag nanotubes

$\varphi = 0$ $\varphi = +2\pi/3$ $\varphi = -2\pi/3$
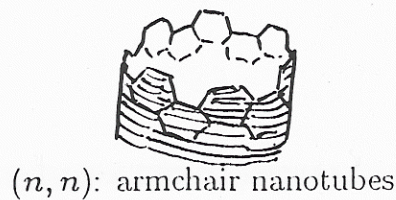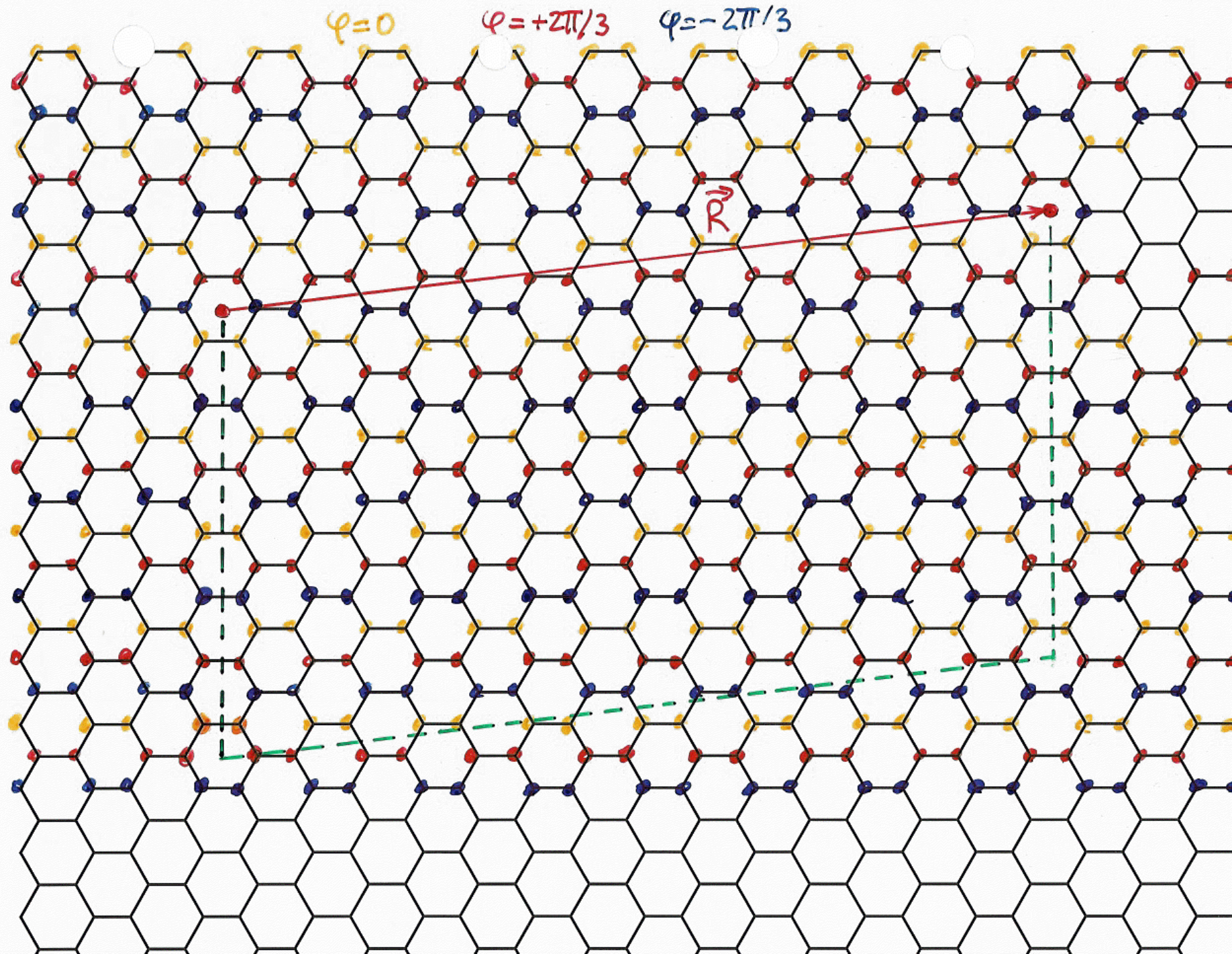
Computational Techniques

- **Total Energy Calculations**

  - *Ab initio* Density Functional Formalism
    * **Plane-wave code** with energy cutoff of 50 Rydbergs
    * Soft nonlocal pseudopotentials and Ceperley-Alder **exchange-correlation** potential
    * 200,000 plane waves in the basis set

  - Parametrized Linear Combination of Atomic Orbitals (LCAO) Formalism
    * Parametrization based on *ab initio* Density Functional results
    * **Very fine k-points mesh** for the inter-tube interaction
    * $O(N)$ technique for **very large systems**
    * Ideally suitable for **massively parallel computation**

  - Tersoff Potential

- **Thermodynamics: Monte Carlo simulations**

- **Time-dependent processes: Molecular dynamics simulations**

- **Transport: Landauer-Büttiker Formalism**

  - Conductance $G(E)$ evaluated by using

$$G(E) = \frac{2e^2}{h} T(E) = \frac{1}{12.9 \text{ k}\Omega} T(E)$$

Thermal Conductivity in Nanotubes

Unusually High Thermal Conductivity of Carbon Nanotubes

Savas Berber, Young-Kyun Kwon,* and David Tománek

Department of Physics and Astronomy, and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824-1116
(Received 23 February 2000)

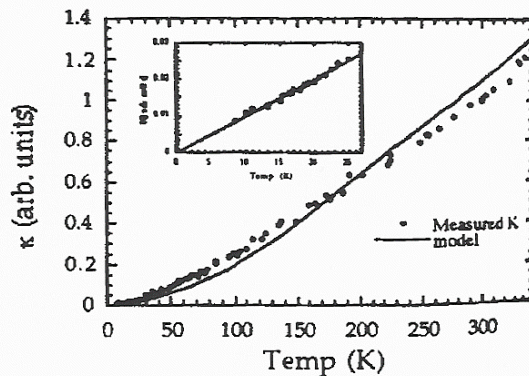$$\frac{1}{A}\frac{dQ}{dt} = -\lambda\frac{dT}{dz}$$

λ = thermal conductivity

$$\lambda \propto C\,v\,l$$

C = heat capacity/volume
v = speed of sound
ℓ = phonon mean free path

λ, T (graph)

- **Experimental Observation for a Nanotube "Mat"**

κ (arb. units) vs Temp (K)

- Measured κ
- model

*J. Hone, M. Whitney, A. Zettl,
Synthetic Metals* **103**, *2498 (1999)*

— Raw data ($T = 300$ K): $\lambda \approx 0.7$ W/m·K

— Extrapolated data ($T = 300$ K): $\lambda \approx 1,800 - 6,000$ W/m·K

R-NT-1869

- **Direct Molecular Dynamics Approach**
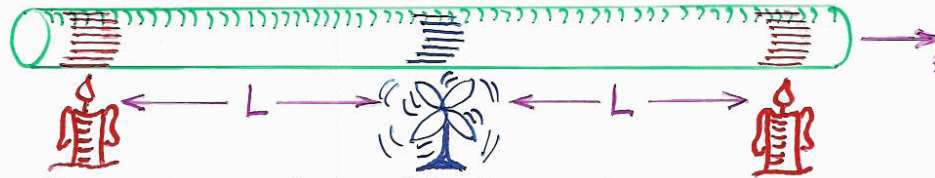
- Temperature profile in a $(10, 10)$ nanotube
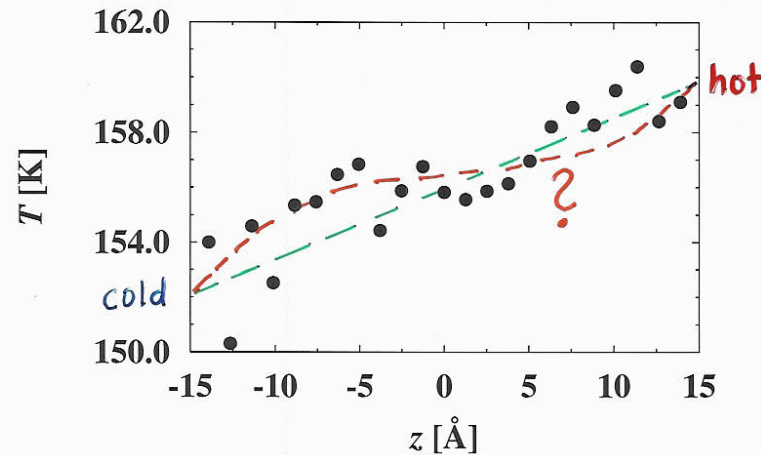
- **Pitfalls of Direct Molecular Dynamics:**

  - $L << l \approx 100$ nm
    $\implies$ velocity rescaling mimics "grain boundary", limits l
  - Large statistical uncertainty
  - $T(z)$ not linear
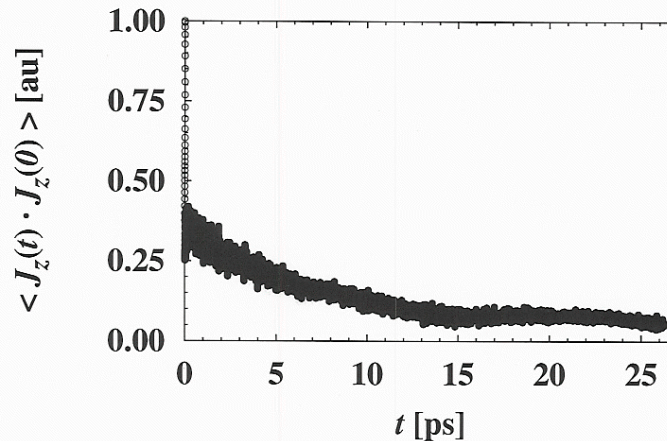 - $dT/dz >> 0 \implies$ spatial variation of thermal conductivity

• Equilibrium Molecular Dynamics Approach

– Green-Kubo formula for the Navier-Stokes thermal conductivity:

$$\lambda = \frac{1}{3Vk_BT^2} \int_0^\infty < \mathbf{J}(t) \cdot \mathbf{J}(0) > dt$$

$$\mathbf{J}(t) = \frac{d}{dt} \sum_i \mathbf{r}_i \Delta e_i = \sum_i \mathbf{v}_i \Delta e_i - \sum_i \sum_{j(\neq i)} \mathbf{r}_{ij}(\mathbf{f}_{ij} \cdot \mathbf{v}_i)$$

– Heat flux autocorreltation function in a $(10, 10)$ nanotube

• Pitfalls of Equilibrium Molecular Dynamics:

– Slow convergence

– Extensive ensemble averaging crucial

– Autocorrelation function requires large data storage

- **Non-Equilibrium Molecular Dynamics Approach**

$$\lambda = \lim_{\mathbf{F}_e \to 0} \tilde{\lambda}(\mathbf{F}_e) \ , \quad \tilde{\lambda}(\mathbf{F}_e) \equiv \lim_{t \to \infty} \frac{< J_z(\mathbf{F}_e, t) >}{F_e T V}$$
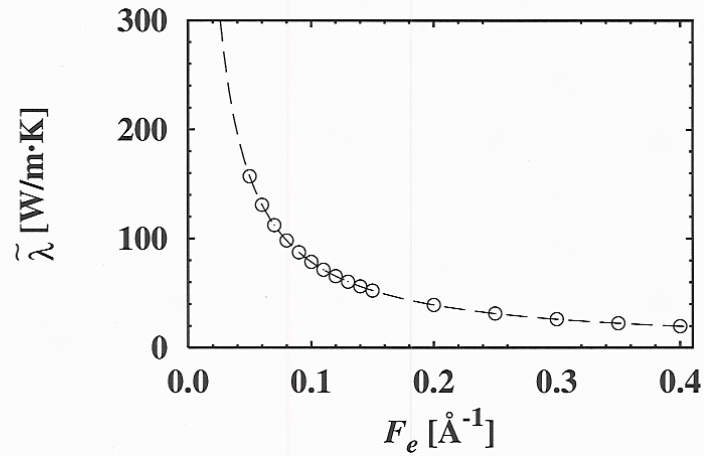
F_e = thermal force, α = Nosé-Hoover thermostat multiplier

$$\Delta\mathbf{F}_i = \Delta e_i \mathbf{F}_e - \sum_{j(\neq i)} \mathbf{f}_{ij}(\mathbf{r}_{ij} \cdot \mathbf{F}_e) + \frac{1}{N} \sum_j \sum_{k(\neq j)} \mathbf{f}_{jk}(\mathbf{r}_{jk} \cdot \mathbf{F}_e) - \alpha \mathbf{p}_i$$

− Axial heat flux in a $(10, 10)$ nanotube for $F_e = 0.2$ Å^{-1}
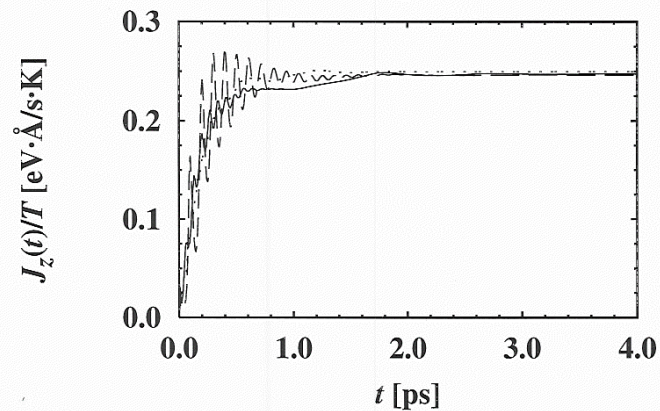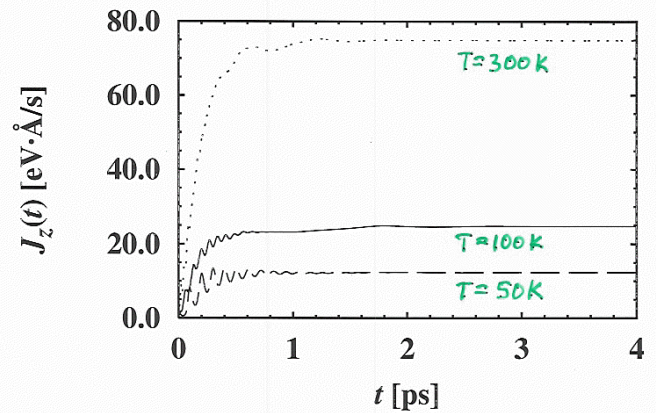
– Heat transport dependence on F_e
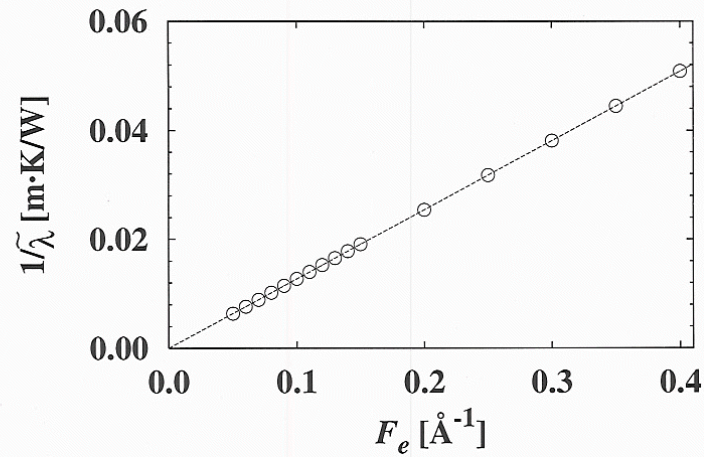
- Pitfalls of Non-Equilibrium Molecular Dynamics:

  – $F_e \rightarrow 0$ limit requires careful evaluation
  – Careful coupling to thermostat required

- Thermal conductivity of an isolated (10,10) carbon nanotube
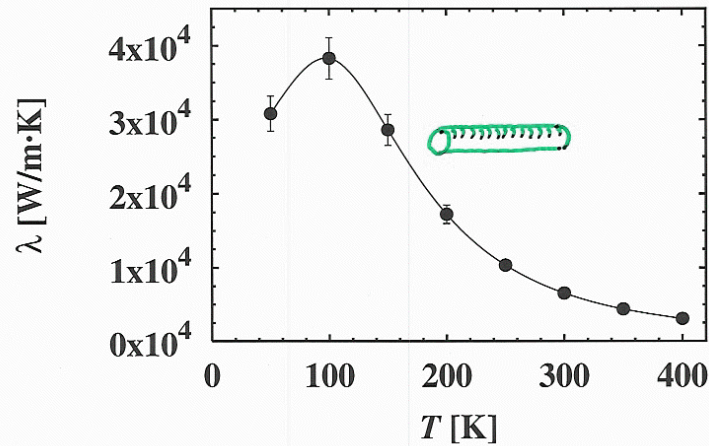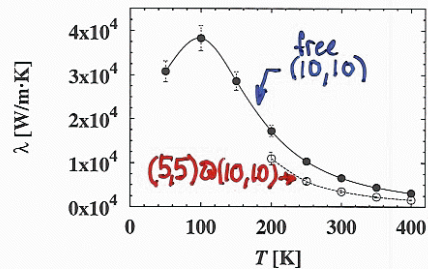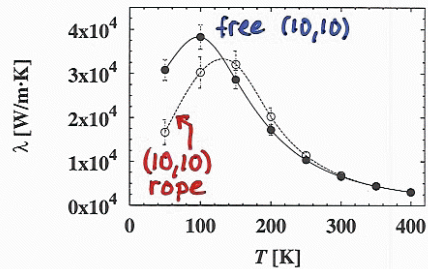

- Thermal conductivity of various carbon allotropes
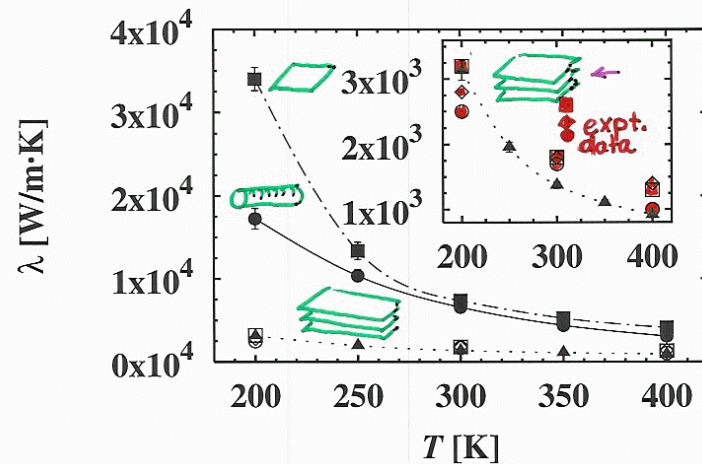
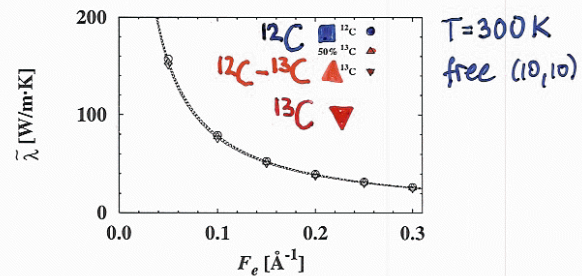▶ **Effect of Inter-Wall Interactions on Thermal Conductivity**

- Thermal conductivity of a
  (5,5)@(10,10) double-wall carbon nanotube

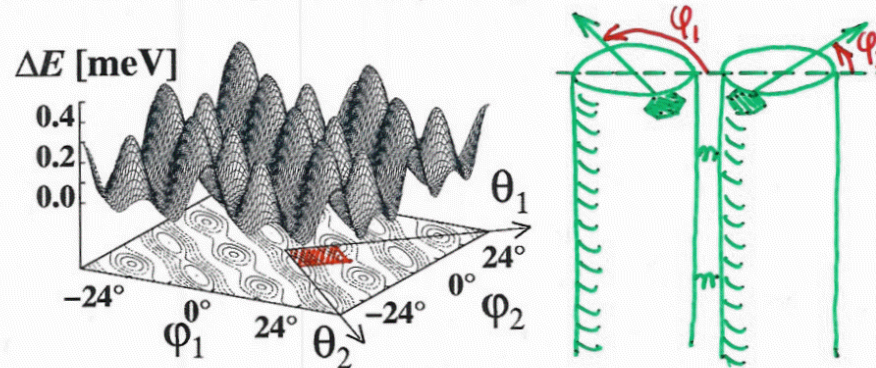- Thermal conductivity of bundled (10,10) nanotubes

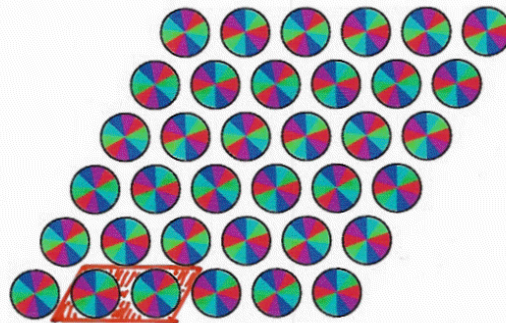▶ **Effect of Isotope Mixture on Thermal Conductivity**

Low-Frequency Phonon Modes
of Nanotubes

▶ **Equilibrium Structure of Bundled and Multi-Wall Tubes**

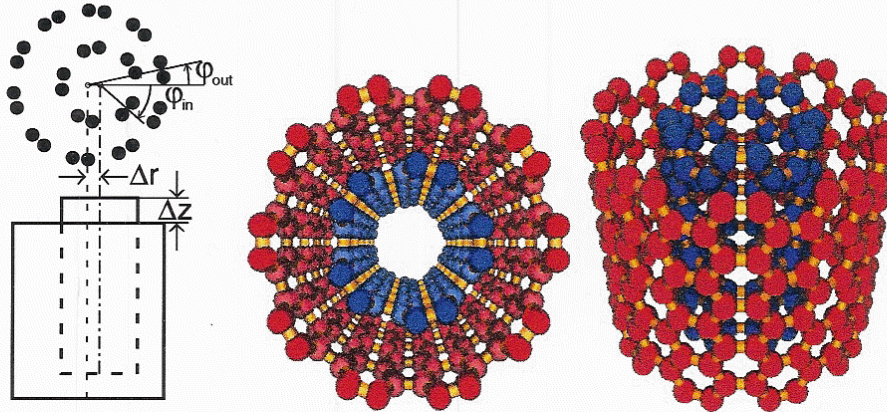• **Interaction between neighboring (10,10) tubes**

• **Equilibrium structure of bundled rigid (10,10) tubes**

– Two-dimensional oblique lattice.

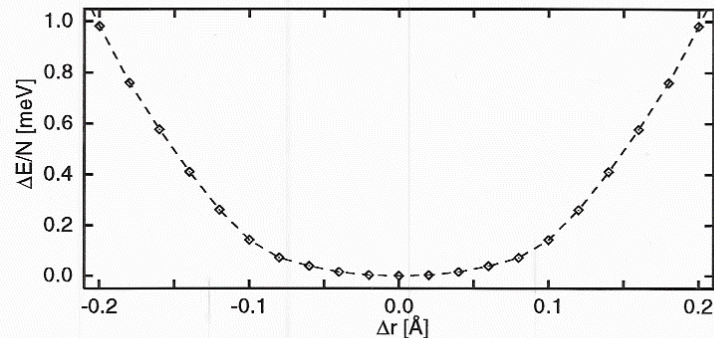- **(5,5)@(10,10) Double-Wall Tube Geometry**

[*Electronic and structural properties of multiwall carbon nanotubes*, Young-Kyun Kwon and David Tománek, Phys. Rev. B **58**, R16001 (1998)]
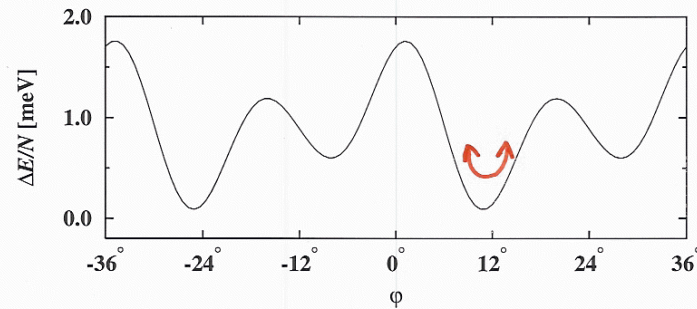

(5,5)@(10,10) Double-Wall Tube

$$\Delta r = 0 \qquad \Delta z = 0$$
$$\varphi_{in} = 0° \qquad \varphi_{out} = 0°$$

– Dependence of Energy on Off-Axis Displacement Δr
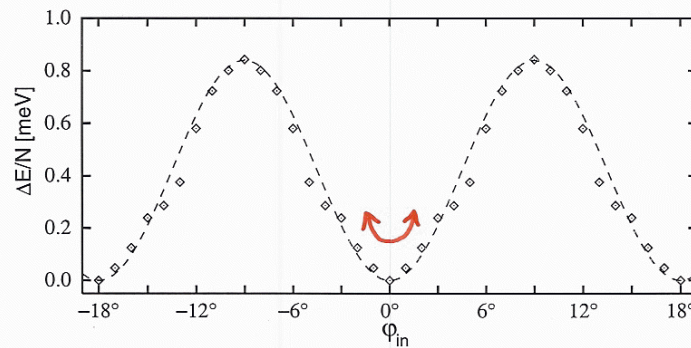
▶ Libration and Rotation Dynamics

- **(10,10) tube "ropes"** [*PRB* **58**, *R13314 (1998)*]

- Librational motion at $T \leq T_{OM}$
- Libration frequency $\nu \approx 12 - 60$ cm^{-1}
- Experimental observation (W. Holmes *et al.*):
  - Infrared modes at $\nu \approx 15, 22, 40$ cm^{-1}
  - These modes disappear at $T \approx 30 - 180$ K

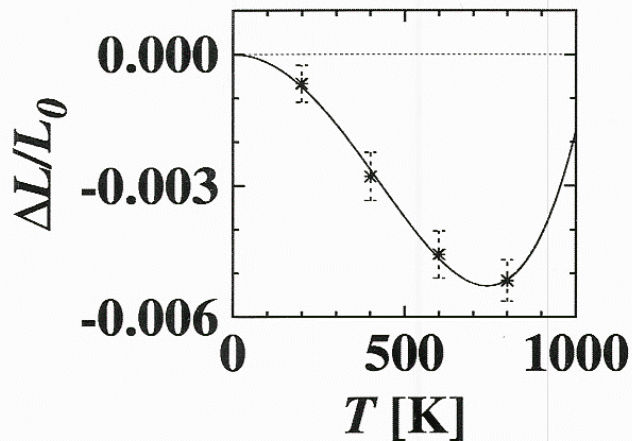- **(5,5)@(10,10) double-wall tube** [*PRB* **58**, *R16001 (1998)*]

- Librational motion at $T \leq T_{OM}$
- Libration frequency $\nu \approx 33$ cm^{-1}

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▶ Soft Phonon Modes of Single-Wall Tubes

L_0

straight

pinch mode

bend mode

$L = L_0 - \Delta L$
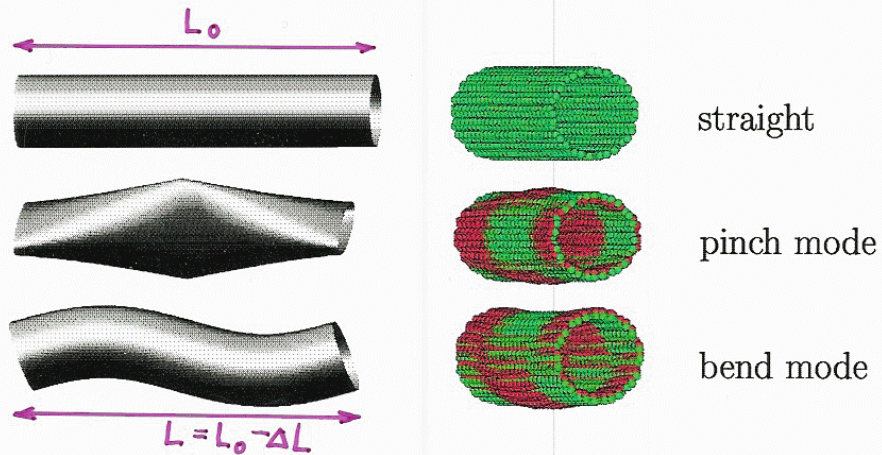
▶ Thermal Expansion of Single-Wall Tubes

$\Delta L/L_0$

0.000

-0.003

-0.006

0   500   1000

T [K]

$\Longrightarrow$ Thermal contraction dominates over bond expansion at low temperatures

▶ Thermodynamics of Orientational Melting
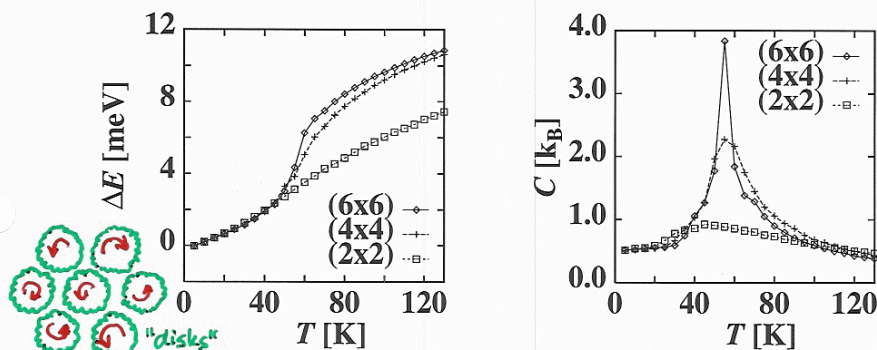
Orientational Melting in Carbon Nanotube Ropes

Young-Kyun Kwon and David Tománek

Department of Physics and Astronomy, and Center for Fundamental Materials Research, Michigan State University,
East Lansing, Michigan 48824-1116
(Received 24 August 1999)

- **Floppy tubes** – unrealistic model
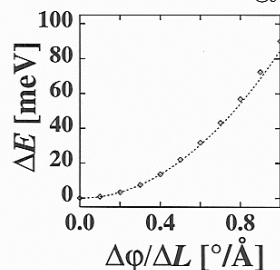 (Torsionally decoupled "layers" within tube)

— Orientational melting at $T_{OM} \approx 55$ K

— Librational motion for $T \lesssim T_{OM}$

— Free rotation at $T \gtrsim T_{OM}$

- **Rigid tubes** – realistic model
  (torsional coupling between "layers" within tube)

— Torsion energy

$$\Delta E_{tor,at}(\Delta\varphi/\Delta L) \approx \kappa \left(\frac{\Delta\varphi}{\Delta L}\right)^2$$

$$\Delta E_{tor,tot}(\Delta\varphi/\Delta L) \sim \frac{1}{\Delta L} \to 0$$
for $\Delta L \to \infty$

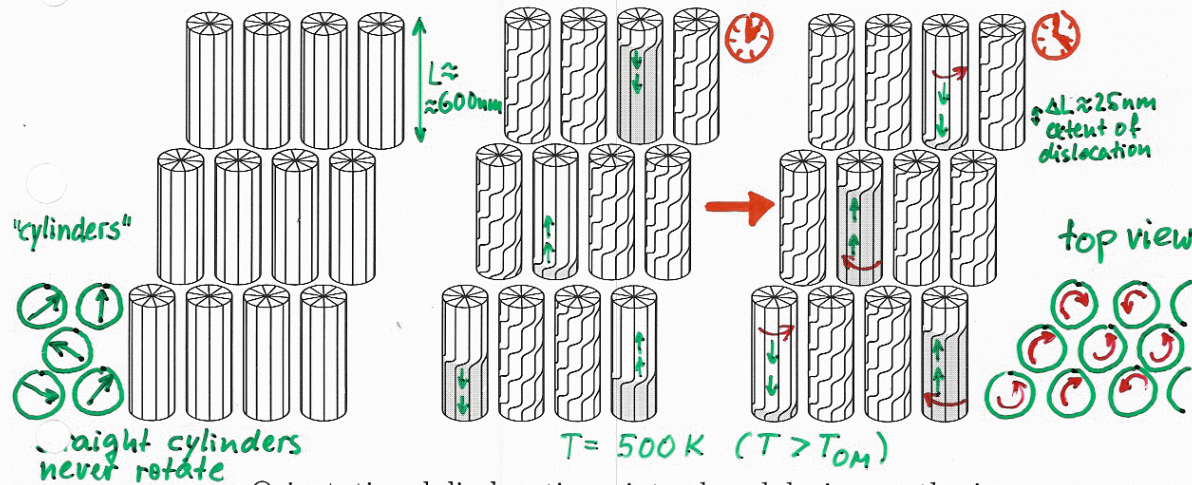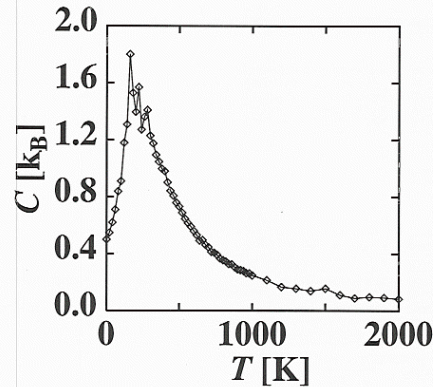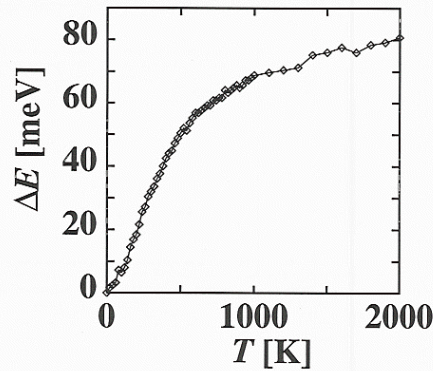* Torsion is thermally activated during synthesis

– Orientational melting

"cylinders"

straight cylinders never rotate

$L \approx 600$ nm

$\Delta L \approx 25$ nm extent of dislocation

$T = 500$ K $(T > T_{OM})$

top view

* Orientational dislocations, introduced during synthesis, are pinned for $T \lesssim T_{OM}$.

* Axial motion of orientational dislocations corresponds to tube rotation.

* Orientational melting, described by free "diffusion" of orientational dislocations along tubes, occurs for $T \gtrsim T_{OM} \approx 100$ K.

* Orientational dislocations (twistons) are scattering centers for electrons $\rightarrow$ strong effect on transport (1D system!).
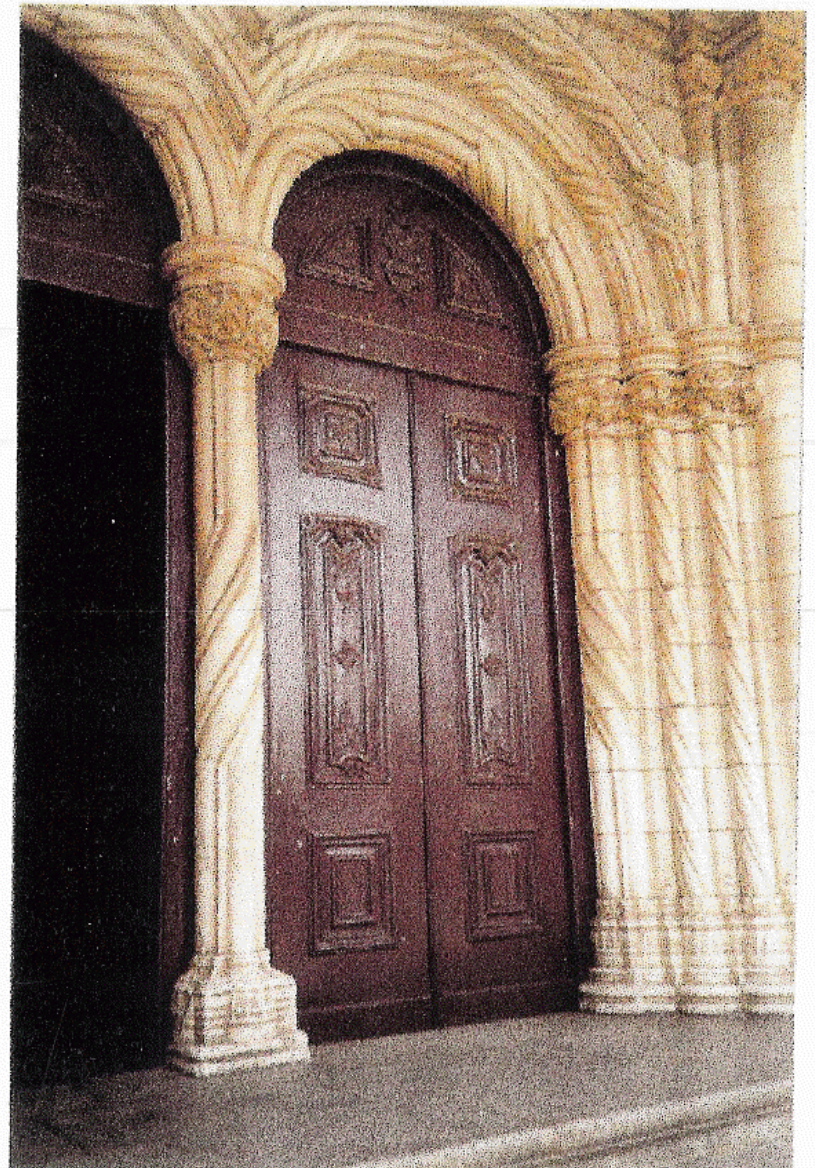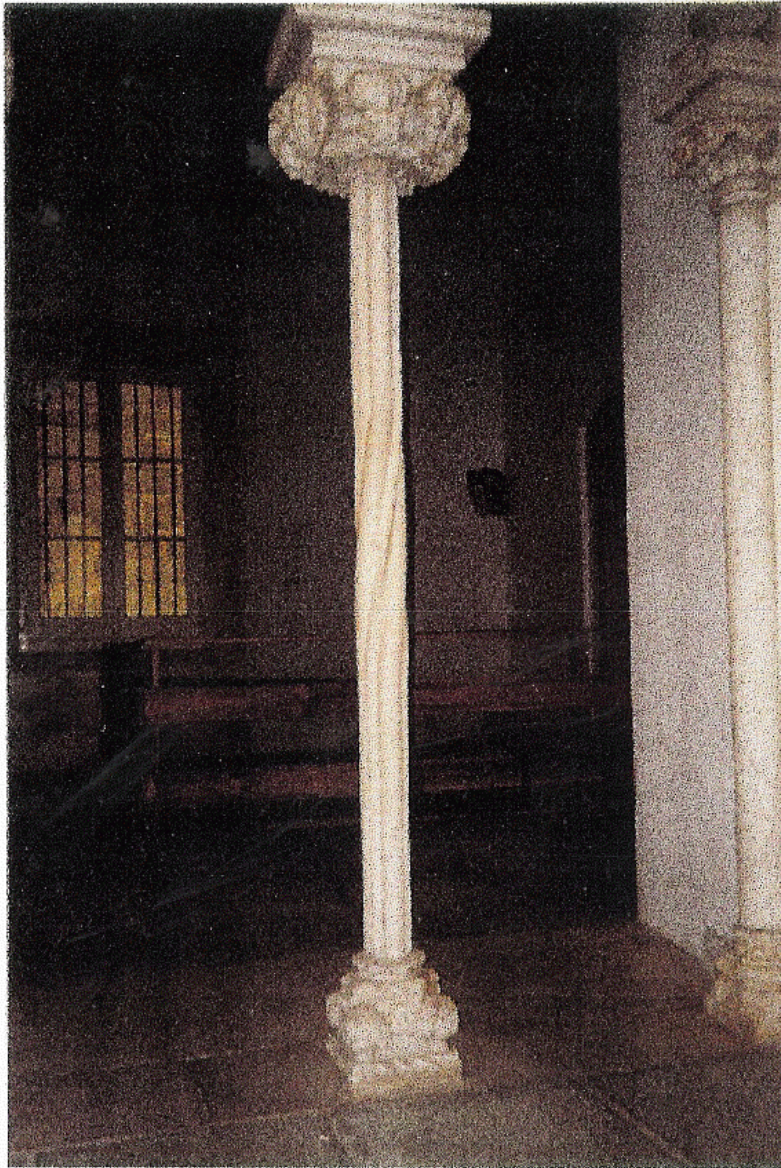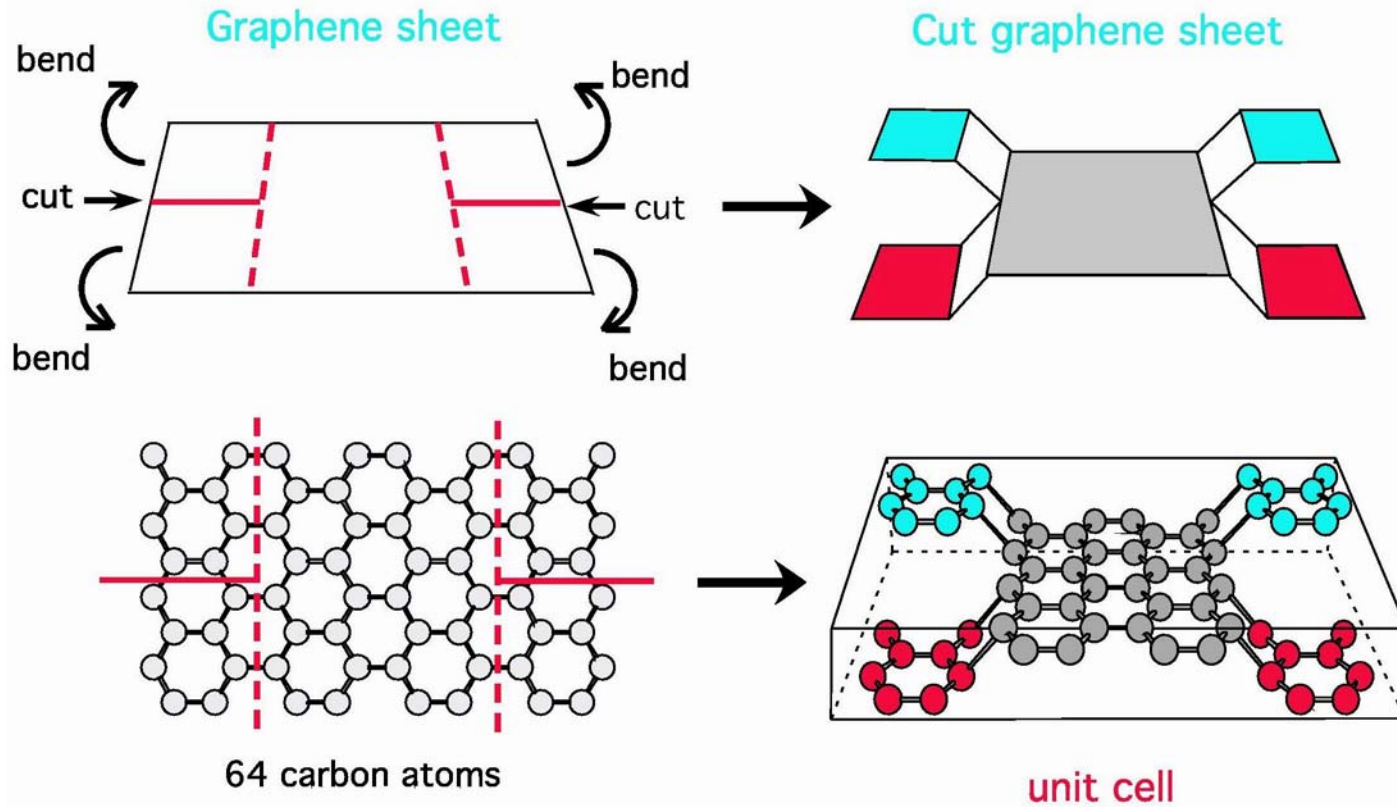
Twistons of Évora (Portugal)
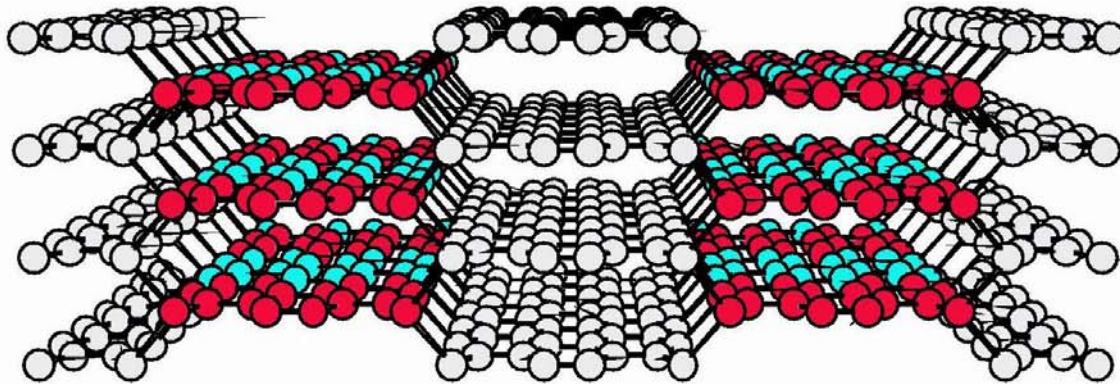
Morphology of Hybrid Graphitic Foam

•**Relationship to graphite**

Graphite

Graphene monolayer

refold...

New Hybrid in-between Diamond and Graphite
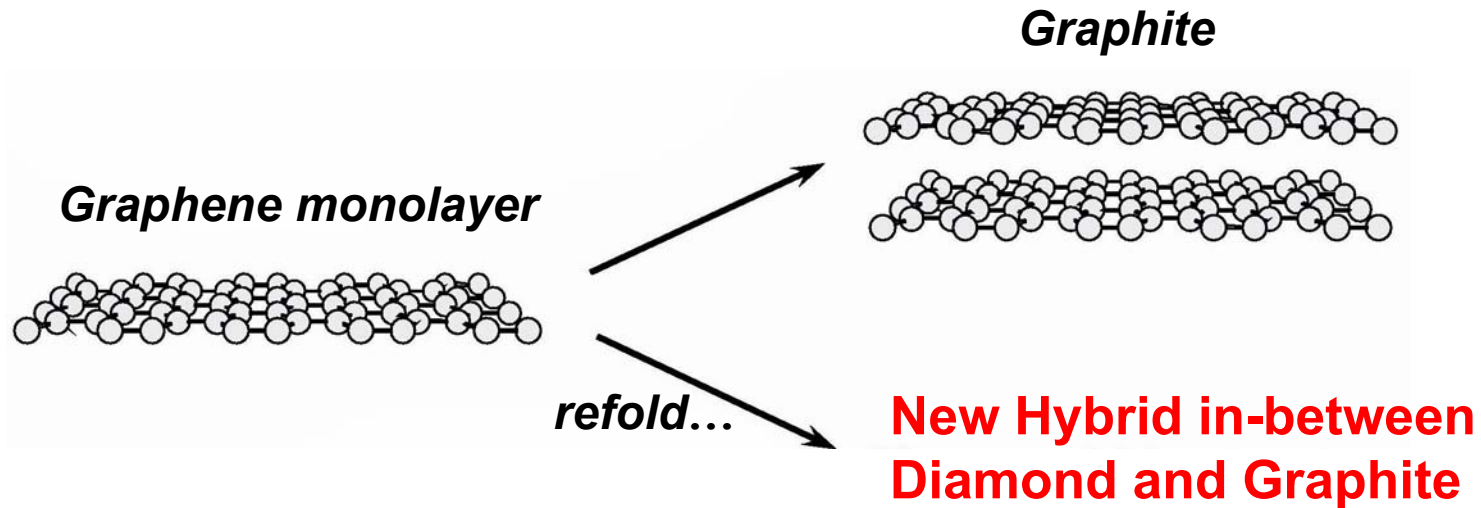
•Folding Process

•Hybrid Graphitic Foam

Terrace size → ∞: graphite
Terrace size → 0: diamond

Present study:
•*Optimized structure*
•*Elastic properties*
•*Electronic structure*

sp² carbon atoms

sp³ carbon atoms

Optimized Structure

a=16.44 Å
b=9.58 Å
c=3.28 Å
ρ = 2.48 g/cm³
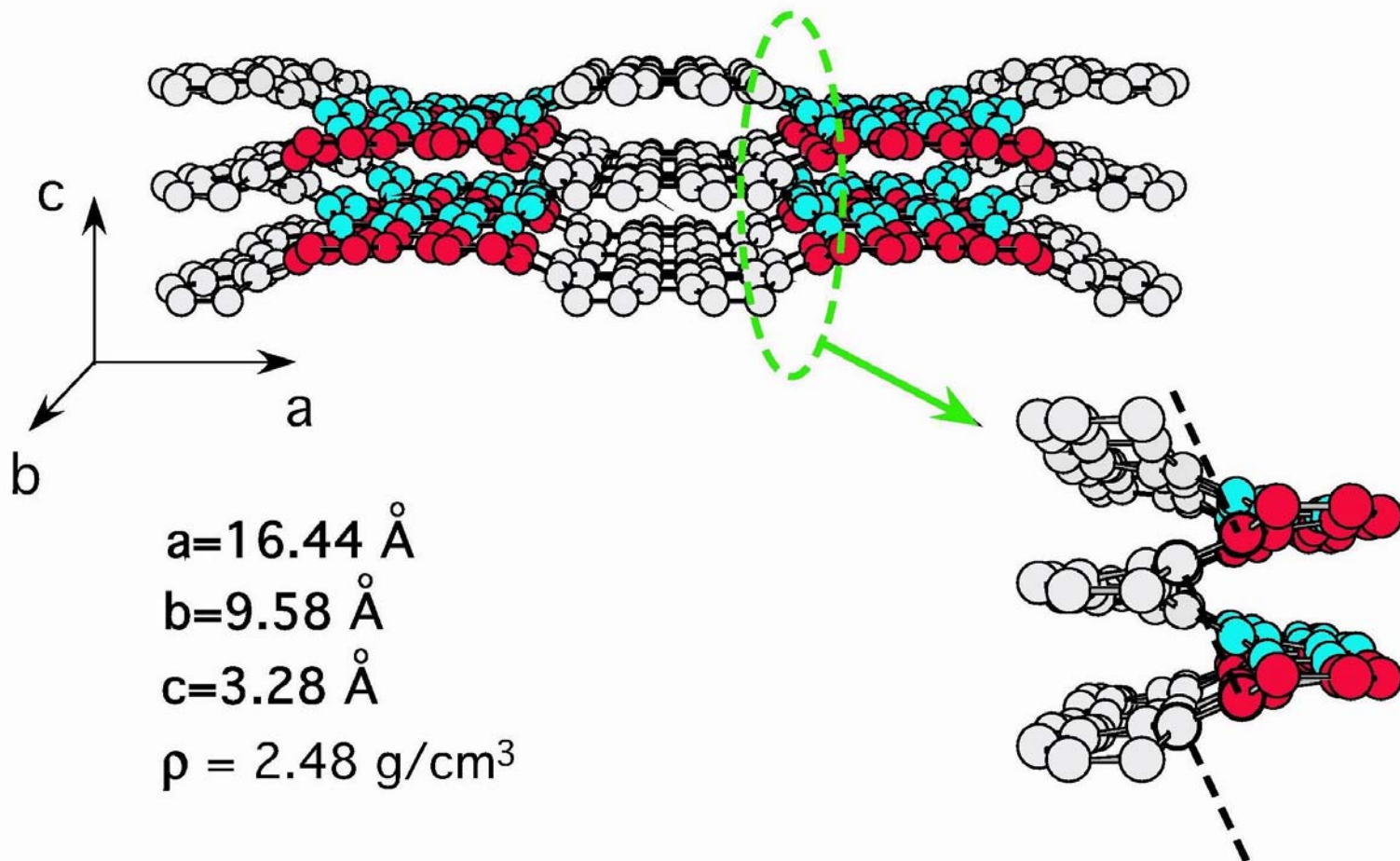
Elastic Properties

	New graphitic foam	Graphite	Diamond
ρ	2.48 g/cm^3	2.27 g/cm^3	3.51 g/cm^3
C_{11} (along a axis)	9.02 Mbar	12.3 Mbar	11.29 Mbar
C_{22} (along b axis)	9.42 Mbar		
C_{33} (along c axis)	0.816 Mbar	0.34 Mbar	
Bulk modulus	0.792 Mbar	0.326 Mbar	4.69 Mbar

Electronic Structure

Brillouin Zone

Band Structure

Density of States
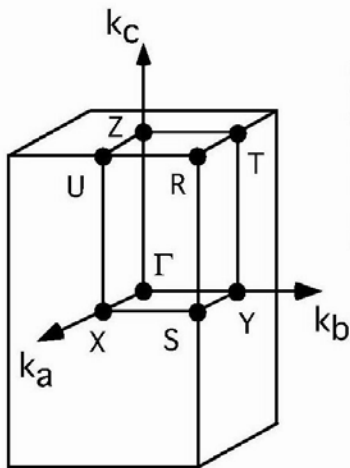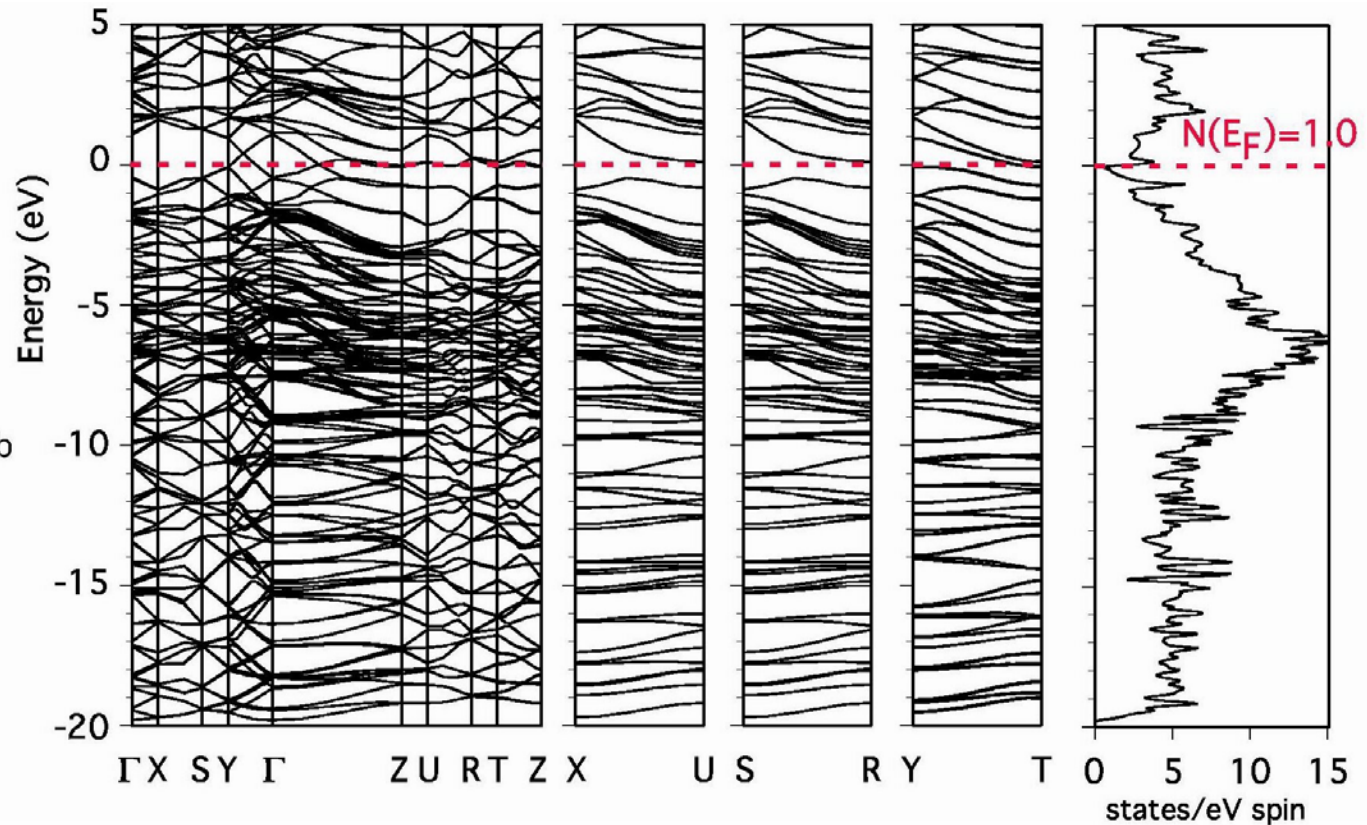
Graphitic foam is metallic: N(E$_F$)=1.0 states/eV/spin

Summary and Conclusions

- We studied the structural rigidity, phonon modes, and thermal conductivity of **carbon nanostructures**: nanotubes and graphitic foam.

- We found that

  - The unusually **high thermal conductance** of nanotubes results from the large phonon mean free path.

  - Weak inter-tube coupling results in a very **soft librational motion**.

  - **Orientational dislocations** are frozen in during the synthesis of interacting nanotubes. Relatively free diffusion motion of orientational dislocations occurs for $T \gtrsim T_{OM} \approx 160$ K, marking the onset of **orientational melting**.

  - **Hybrid graphitic foam** offers an **unsusual combination of properties**: low mass density, high structural rigidity, possibly high electric and thermal conductivity.